



Effect of Ultraviolet Absorbing Agents on Photodegradation Behavior of a Disperse Dye

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ABSTRACT

The action and effect of ultraviolet absorbing agents (UVA) on the photofading of dyed fiber, in particular polyester, were investigated using a monochromatic light source. Polyester fiber itself and the dyed fiber were affected markedly by spectroirradiation at a specific wavelength, viz. 316 nm: yellowing of the fiber alone and photofading of C.I. Disperse Red 73 on the fiber occurred maximally at this wavelength. UVAs of the benzotriazole and phenyl salicylate types, which show absorption spectra around 316 nm, protected the decomposition of polyester at 316 nm irradiation, and hence the photodegradation of the dye on the fiber. Diacetate and triacetate fibers were decomposed maximally by irradiation at 230 nm and 259 nm, respectively. These wavelengths also affected the photodegradation of the disperse dye on the fibers. A UVA which does not absorb light below 260 nm was found not to be operative for improving the photodegradation of the fibers themselves and of the dye on the fibers. The relationship between the added UVA and the photodegradation behavior of the fiber and of the dyed fiber is discussed. © 1997 Elsevier Science Ltd

Keywords: ultraviolet absorbing agent, polyester, disperse dye, photofading, spectroirradiation.

INTRODUCTION

In previous papers the photodegradation of some azo and anthraquinone disperse dyes on fibers such as polyester, nylon, diacetate, and triacetate was

investigated using a monochromatic light source divided into 20 specific wavelengths from 200 nm to 700 nm, instead of the light involving the whole wavelength range [1, 2]. The photodegradation behavior at each wavelength was examined. The fibers themselves were influenced remarkably at specific wavelengths, viz. yellowing of the fibers occurred maximally at 316 nm for polyester, at 372 nm for nylon, at 230 nm for diacetate, and at 259 nm for triacetate. The photofading of the disperse dyes on the fiber took place maximally at the corresponding wavelength. The largest effect on the photodegradation is a specific fiber–wavelength combination. Thus it is likely that the photodegradation of the dye on the fiber is significantly affected by the absorbed energy characteristic of the fiber and/or degradation products of the fiber formed at the specific wavelength. As a general rule, this trend was observed for synthetic fiber–disperse dye and cotton fiber–reactive dye systems [1, 2].

It is known that polyester fiber dyed with disperse dyes shows high light fastness compared with the other fibers dyed with disperse dyes or other kinds of dyes. The polyester–disperse dye system is useful and practical in cases where high light fastness is required, such as for example, in the system commonly used for automotive interiors and seats. For this purpose it is essential to produce dyed fabrics with excellent light fastness. In order to improve the light fastness, ultraviolet absorbing agents are often employed during dyeing.

In this investigation the action and effect of ultraviolet absorbing agents have been studied using a monochromatic light source and the same technique as that used in the previous articles [1, 2].

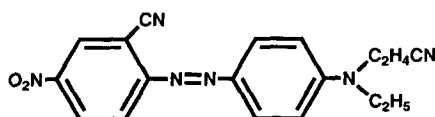
EXPERIMENTAL

Materials

Sumikaron Rubine SE-GL (C.I. Disperse Red 73, Sumitomo Chemical Co., Ltd.), which is a typical azo disperse dye, was used as a representative dye. The structure is shown in Fig. 1. Commercial grade dye was employed without further purification for the dyeing of polyester, diacetate, and triacetate fibers. The polyester (Tetrontropical, Toray Co., Ltd.), diacetate (Linda, Mitsubishi Rayon, Co., Ltd.), and triacetate (Soalon, Mitsubishi Rayon, Co., Ltd.) fibers were utilized after scouring. For dyeing polyester, diacetate, and triacetate, a commercial grade sample of anionic surfactant, Sumipon TF (Sumitomo Chemical Co., Ltd.) was added. The structures of the three ultraviolet absorbing agents, Sumisorb 250, 300, and 400 (Sumitomo Chemical Co., Ltd.), which are designated UVA 1, UVA 2, and UVA 3, respectively, are shown in Fig. 2.

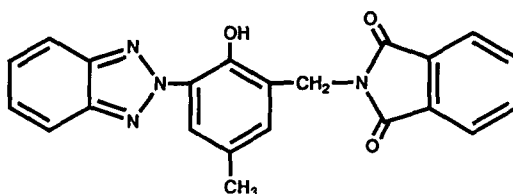
Dyeing of polyester

The dyebath (180 ml) contained the disperse dye, the anionic surfactant (0.2 g), and acetate buffer (0.2 g of sodium acetate and 0.05 g of acetic acid, pH 5). The dye concentration was calculated to correspond to a 1/1 shade (JIS). Polyester fiber (5 g) was immersed in the dyebath at 60°C and the temperature was raised from 60°C to 130°C. Dyeing was continued for

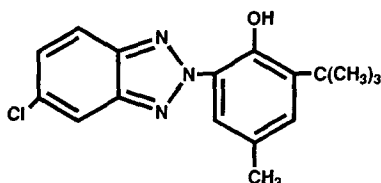


C.I. Disperse Red 3

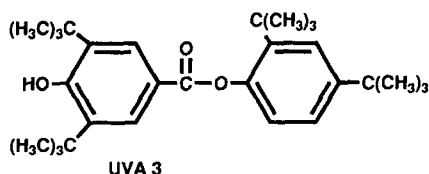
Fig. 1. The structure of dye used.



UVA 1



UVA 2



UVA 3

Fig. 2. The structure of ultraviolet absorbing agents used.

30 min at 130°C, the temperature was then reduced to 60°C, and rinsing was carried out. After dyeing a reduction clearing treatment was done.

Dyeing of diacetate

Diacetate fiber was dyed by the same method as that of polyester fiber. With diacetate fiber the dyeing was carried out at 85°C for 60 min.

Dyeing of triacetate

The method of dyeing triacetate fiber was essentially the same as that for polyester fiber. Triacetate fiber was dyed at 120°C for 10 min.

Treatment of ultraviolet absorbing agent (UVA)

The UVA was dispersed using a nonionic surfactant. Either before starting the dyeing or during the dyeing process, the dispersed UVA was added to the dyebath containing the disperse dye and synthetic fiber, or the synthetic fiber alone. After dyeing, reduction clearing treatment was carried out.

Apparatus

A spectroirradiator (CRM-FA, JASCO Co., Ltd.) used in this experiment was the same as that employed in the previous experiments [1, 2]; the outline of the apparatus was presented in detail in the previous paper [1]. The light source was a xenon lamp of 2 kW (UXL-2003D, Ushiodenki Co., Ltd.). The lamp covered all wavelengths from 200 nm to 700 nm. The light was divided into twenty single wavelengths of 201, 230, 259, 288, 316, 344, 372, 399, 426, 453, 479, 505, 531, 556, 581, 606, 630, 654, 678, and 701 nm by the diffraction lattice. The fibers mounted in the twenty sample rooms were irradiated by the monochromatic light of each wavelength.

Measurements of photodegradation

The coloration, i.e. yellowing of synthetic fiber itself, and the color change of the dye on the fiber, were evaluated by color difference (ΔE) using a Macbeth Color-Eye 3000 (Sicomuc 20, Sumika Chemical Analysis Service Co., Ltd.).

Measurements of absorption spectrum of UVA

The spectrum of UVA in DMF was measured by a UV-VIS spectrophotometer (UVPC-3101, Shimazu Co., Ltd.).

Measurements of UVA on fiber

UVA on the fiber was extracted by 90% DMF. The concentration of extracted UVA in 90% DMF was measured using a UV-VIS Spectrophotometer (UVPC-3101, Shimazu Co., Ltd.).

RESULTS AND DISCUSSION

The effect of three ultraviolet absorbing agents, UVA 1, UVA 2, and UVA 3, on the light fastness of C.I. Disperse Red 73 has been examined. UVA 1 and UVA 2 are of the benzotriazole type and UVA 3 is a phenyl salicylate type. These UVAs were developed for improving the light fastness of disperse dyes on polyester fiber. The degree of exhaustion of UVA for polyester, diacetate, and triacetate fibers is shown in Table 1. As is apparent in Table 1, UVA 1, UVA 2, and UVA 3 exhibit an excellent degree of exhaustion for polyester. However, it was found that whilst UVA 3 is not exhausted at all by diacetate and triacetate, UVA 1 and UVA 2 show considerable exhaustion on triacetate. The degree of exhaustion thus depends on the structures both of the UVA and of the fibers.

The absorption spectra of the UVAs are shown in Fig. 3. UVA 1 and UVA 2 show a similar absorption spectrum from *ca.* 260 nm to *ca.* 400 nm. In contrast, UVA 3 exhibits two main peaks at *ca.* 280 nm and *ca.* 350 nm.

Polyester, diacetate, and triacetate fibers and fibers dyed with C.I. Disperse Red 73 were irradiated by the spectroirradiator by which a monochromatic light source divided into twenty single wavelengths from 200 nm to 700 nm can be applied. The changes in color of polyester fiber itself and of the dyed fiber are shown in Fig. 4 as a typical example. In Fig. 4 the color change *i.e.*, yellowing of the fiber itself or fading of the dyed fiber is expressed as a function of the color difference, ΔE between the original and the irradiated fibers. Figure 4 suggests that the color change or fading occurs maximally around 316 nm for polyester and is dependent on the irradiation wavelength. The maximum change appeared at 230 nm for diacetate (Fig. 5) and 259 nm for triacetate (Fig. 6). The largest effect on the photodegradation is a specific

TABLE 1
Degree of Exhaustion of Ultraviolet Absorbing Agents for Fibers

<i>Fiber</i>	<i>Degree of exhaustion (%)</i>		
	<i>UVA 1</i>	<i>UVA 2</i>	<i>UVA 3</i>
Polyester	60.4	69.2	57.9
Diacetate	12.3	29.9	0
Triacetate	31.7	55.0	0

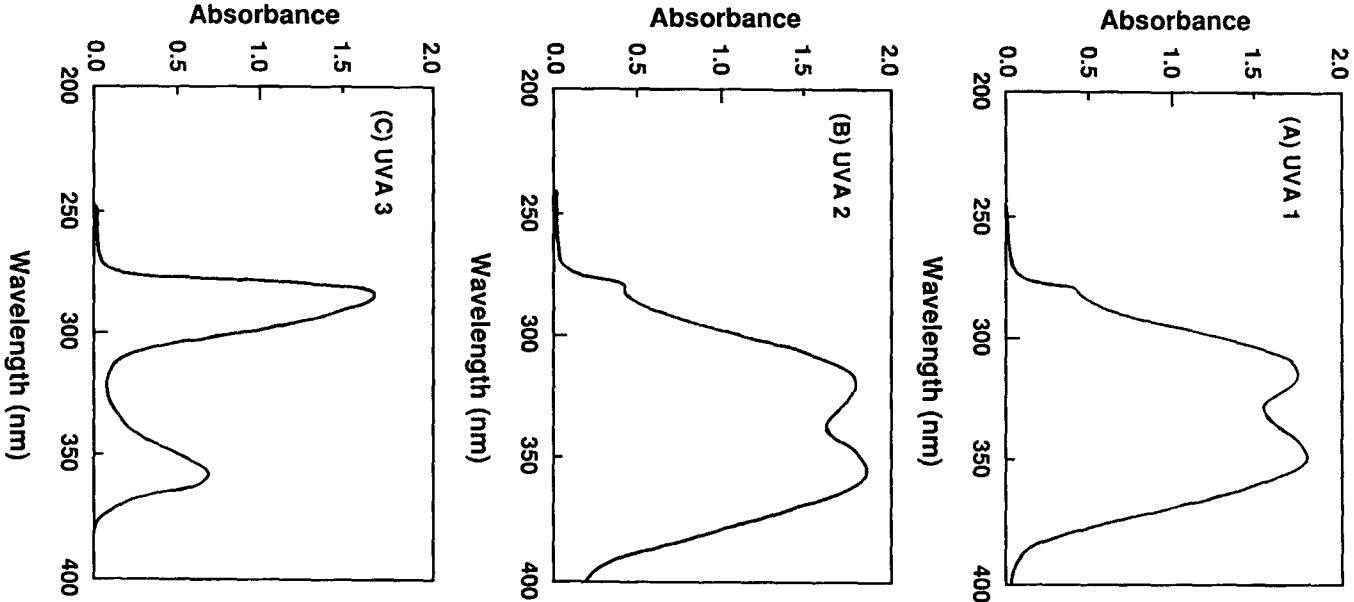


Fig. 3. The spectra of ultraviolet absorbing agents used: (A) UVA 1, (B) UVA 2, (C) UVA 3

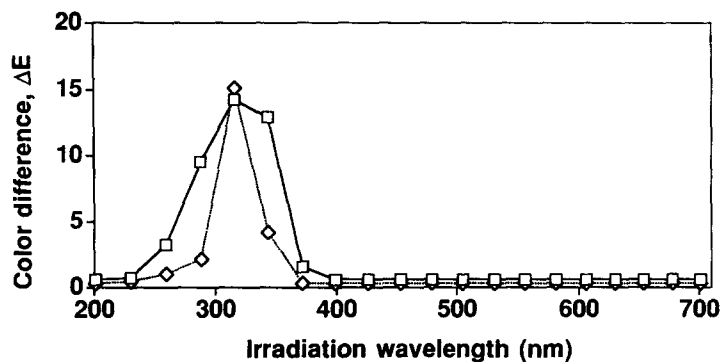


Fig. 4. Color change of undyed and dyed polyester fibers by spectroirradiation: (□) undyed polyester, (◇) dyed polyester with C.I. Disperse Red 73. Irradiation energy; 290 kJ/cm².

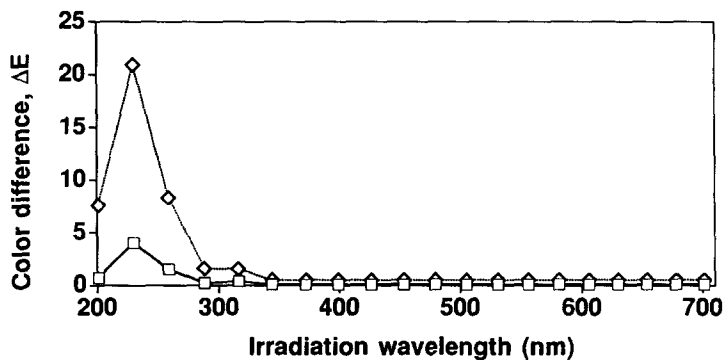


Fig. 5. Color change of undyed and dyed diacetate fibers by spectroirradiation: (□) undyed diacetate, (◇) dyed diacetate with C.I. Disperse Red 73. Irradiation energy; 290 kJ/cm².

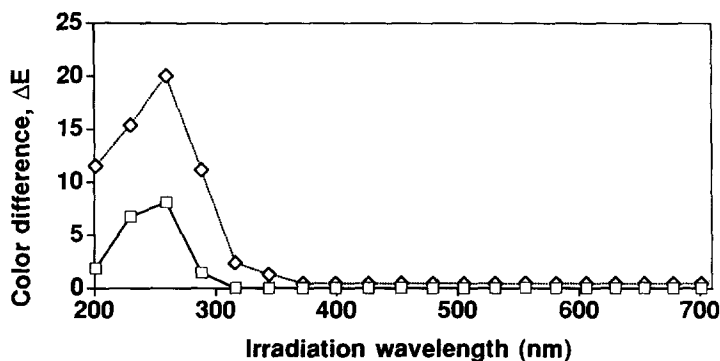


Fig. 6. Color change of undyed and dyed triacetate fibers by spectroirradiation: (□) undyed triacetate, (◇) dyed triacetate with C.I. Disperse Red 73. Irradiation energy; 290 kJ/cm².

fiber–wavelength combination. These situations have been reported already in detail in the previous papers [1, 2].

The effect of added UVA on the color change of polyester fiber itself has been investigated. The results are shown in Fig. 7. For purpose of comparison, the degree of exhaustion of UVA 1, UVA 2, and UVA 3 was adjusted to be the same by controlling the concentration of UVA in the dyebath, to ensure the fiber contained the same amount of UVAs. As is apparent in Fig. 7, the color difference, ΔE is decreased appreciably by the addition of UVA at 316 nm, suggesting that UVA depresses yellowing and hence decomposition of the fiber itself. This is presumably due to the strong absorption around 316 nm by these UVAs, in particular UVA 1 and UVA 2, as illustrated in Fig. 3. The effectiveness increases in the following order at 316 nm: UVA 3, UVA 1, UVA 2.

Figure 8 shows the photodegradation behavior of polyester dyed with C.I. Disperse Red 73 in the presence and absence of UVA. Figure 8 shows that the dyed fibers are influenced maximally at 316 nm, i.e. as the undyed fiber, in spite of the presence and absence of UVA. However, the color difference at 316 nm is considerably decreased by the presence of UVA, indicating that UVA suppresses the photofading of dye on polyester. The effectiveness is in the order, UVA 2 \approx UVA 1 > UVA 3, although the difference in effectiveness is small among these three UVAs. Thus it is evident from Figs 7 and 8 that the addition of UVA depresses the fading of dye on the fiber as well as the yellowing of the fiber itself at 316 nm. It is of interest in Fig. 7 that a little increase of ΔE is observed below 288 nm. This means that the decomposition of the fiber is enhanced slightly by irradiation below 288 nm. Correspondingly, the photofading of dye on the fiber is accelerated very slightly below 288 nm, as shown in Fig. 8. However, in any event, it is evident that

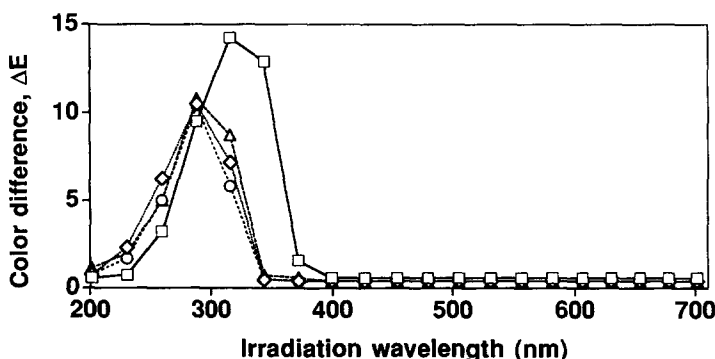


Fig. 7. Effect of ultraviolet absorbing agents on decomposition of polyester fiber: (□) none, (◇) UVA 1, (○) UVA 2, (△) UVA 3. Irradiation energy; 290 kJ/cm^2 .

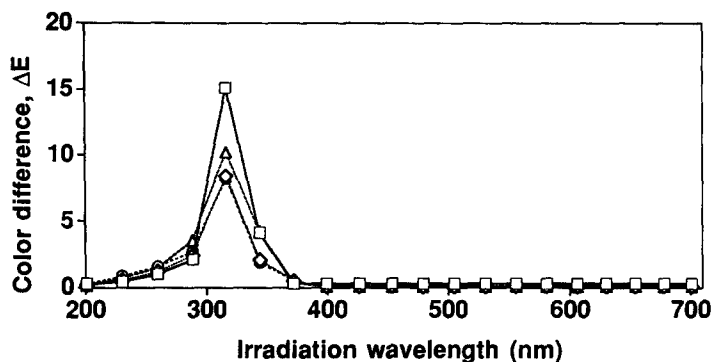


Fig. 8. Effect of ultraviolet absorbing agents on decomposition of C.I. Disperse Red 73 on polyester fiber: (□) none, (◇) UVA 1, (○) UVA 2, (△) UVA 3. Irradiation energy; 290 kJ/cm².

substantial photodegradation of the undyed and dyed fibers at 316 nm is suppressed appreciably by the added UVA.

A mechanism of decomposition of polyester by ultraviolet light in the presence and absence of oxygen has been proposed by Day and Wiles [3, 4]. In the absence of oxygen, the main chain of polyester is radically split by light, and a hydrogen abstraction reaction and Norrish II type reaction occur. In the presence of oxygen the elimination reaction of carbon dioxide produces hydroxyperoxide and its decomposition products react with a hydrogen atom of the phenylene ring in polyester, forming monohydroxyphthalate. Also a mode of action of ultraviolet absorbing agents for depressing decomposition of polyester was presented by Newland and Tamblyn [5]. When the ultraviolet absorbing agents of the benzophenone or benzotriazole type absorb UV light, tautomerism occurs in the excited state and the tautomers revert to the stable and ground state, liberating energy.

The photodegradation of dye on polyester fiber might arise from the absorbed energy characteristic of the fiber and/or degradation products of the fiber formed at the characteristic wavelength. In Fig. 7 the decrease in E of polyester itself in the presence of UVA demonstrates strongly the decrease in decomposition of the polyester matrix. As shown in Figs 7 and 8, the added UVA inhibits the degradation of polyester itself and hence the photofading of dye on the fiber. Accordingly, from the results obtained here it is very likely that the fading of the dye on the fiber is governed predominantly by the degradation products of the polymer rather than the absorbed energy characteristic of the fiber.

In order to clarify and confirm the above situation, the photodegradation of C.I. Disperse Red 73 on diacetate and triacetate fibers was checked in the presence and absence of UVA. In this case, UVA 2 was employed because

this UVA was uptaken appreciably by the fibers. As shown in Fig. 5, the color change of undyed and dyed diacetate fibers by spectroirradiation occurs maximally at 230 nm. Figure 9 illustrates the effect of added UVA 2 on the decomposition of diacetate fiber alone. It is obvious that the most effective wavelength for the photodegradation of diacetate is near 230 nm. Ultraviolet irradiation of 230 nm mainly leads to a photochemical reaction and decomposes the matrix. The addition of UVA 2 is not at all effective in preventing decomposition of the fiber, though the UVA is incorporated in the matrix as shown in Table 1. This is probably due to the fact that UVA 2 has no absorption near 230 nm (Fig. 3). The photofading behavior of the dye on diacetate is illustrated in Fig. 10, where the photofading also occurs maximally near 230 nm. Figures 9 and 10 show that with diacetate the ΔE value does not change at the maximal wavelength, even if the UVA is

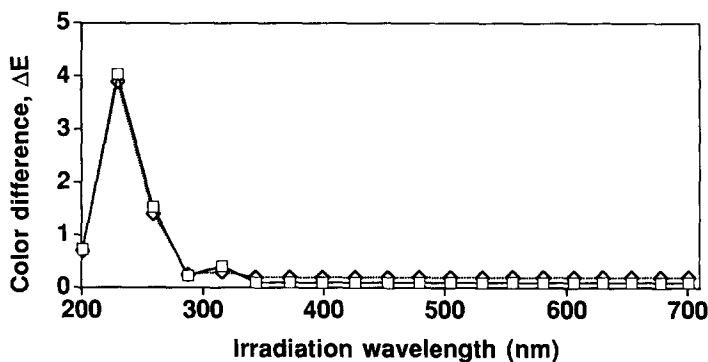


Fig. 9. Effect of ultraviolet absorbing agent on decomposition of diacetate fiber: (□) none, (◇) UVA 1. Irradiation energy; 290 kJ/cm².

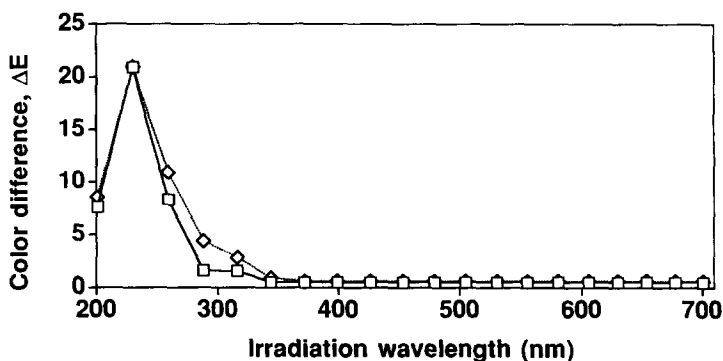


Fig. 10. Effect of ultraviolet absorbing agent on decomposition of C.I. Disperse Red 3 on diacetate fiber: (□) none, (◇) UVA 1. Irradiation energy; 290 kJ/cm².

exhausted to the fiber. Neither the fiber nor the dye on the fiber is affected by the added UVA. This situation is different from that of polyester. These results imply that the UVA is not able to prevent the decomposition of diacetate and hence the UVA is not effective in improving light fastness of the dye on the fiber. In other words, the degradation products of the fiber formed at the characteristic wavelength play a significant role in the photofading of the dye on the fiber.

The photodegradation behavior of C.I. Disperse Red 73 on triacetate fiber is depicted in Figs 6, 11 and 12. With triacetate the same phenomena as those of diacetate were observed: the photodegradation of both undyed and dyed triacetate fibers was not improved in spite of the presence of UVA. It is likely that when the UVA cannot restrain the decomposition of fiber matrix, the UVA does not work effectively in decreasing the fading of dye in the matrix.

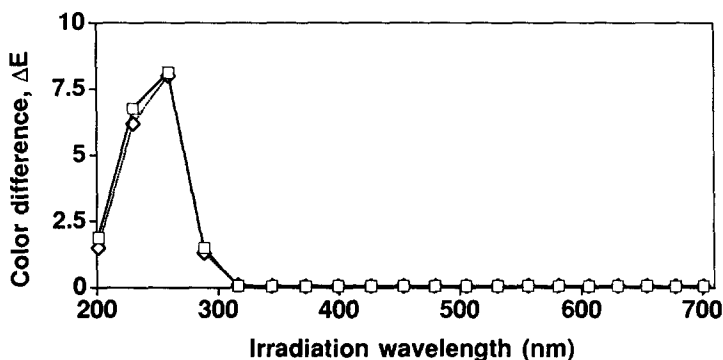


Fig. 11. Effect of ultraviolet absorbing agent on decomposition of triacetate fiber: (□) none, (◇) UVA 1. Irradiation energy; 290 kJ/cm².

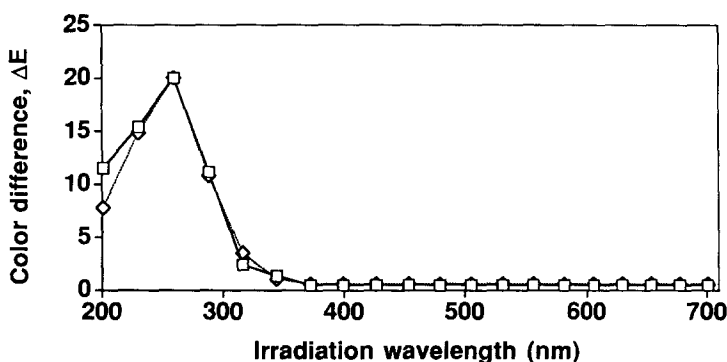


Fig. 12. Effect of ultraviolet absorbing agent on decomposition of C.I. Disperse Red 73 on triacetate fiber: (□) none, (◇) UVA 1. Irradiation energy; 290 kJ/cm².

CONCLUSION

It was found that polyester, diacetate, and triacetate fibers undergo photodegradation at specific wavelengths, viz. 316 nm, 230 nm, and 259 nm, respectively. A disperse dye on the fibers was also affected maximally at the corresponding wavelength. Three kinds of ultraviolet absorbing agents (UVA) used in this experiment absorbed light above 260 nm and were exhausted by polyester. The exhaustion of the UVA to polyester prevented yellowing of the polymer matrix from irradiation at 316 nm. Also the photofading of the dye on the fiber was decreased by the added UVA. In contrast, the photodegradation of diacetate or triacetate alone and the dye on the fiber was not improved at all by the UVA. These results imply that the light fastness of a dye on fiber is increased significantly by the addition of UVA when the UVA can prevent photodegradation of the fiber itself at a specific wavelength of irradiation.

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